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Deuterium retention and release from highly irradiated annealed tungsten after exposure to a deuterium DC glow discharge

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Abstract

Samples from tungsten rods irradiated by 800 MeV protons in the Los Alamos Neutron Science Center have been used in experiments to study the effects of radiation damage and annealing on the retention of hydrogen isotopes. These samples were annealed and then exposed to deuterium ions using a DC glow discharge. Following exposure, the samples were subjected to a linear temperature ramp from ~300 to ~1500 K, and the offgas analyzed by mass spectrometry. The results indicate that annealing to a temperature of only 1273 K for 6 h effectively removed all irradiation-produced traps, and that hydrogen trapping at voids is not as prevalent as had been assumed. Modeling the deuterium release suggests that most of the trapping occurred in near-surface 1.4 eV traps, in a low concentration of uniform 1.4 eV traps, and in 0.95 eV traps likely resulting from oxygen diffusion from the original water-cooled irradiation environment.
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1. Introduction

Tungsten will be used as the primary material in the divertor of the International Thermonuclear Experimental Reactor (ITER), and is a candidate for use in future, energy producing, fusion reactors. As a plasma facing material, the tungsten will be exposed to high fluences of energetic deuterium and tritium. If the retention of the tritium is high, safety concerns will be generated by the use of this material.

Numerous experiments on the retention of hydrogen isotopes in tungsten [1–7] have suggested that tungsten will not retain large quantities of tritium if used as a plasma facing material. With all materials, however, there is still the concern that radiation damage from the high-energy fusion neutrons could result in significant trapping of tritium. In an earlier report [8], we examined the protium release from tungsten that had been irradiated by 800 MeV protons in the Los Alamos Neutron Science Center (LANSCE) beam line. Those experiments showed the high-energy protons to generate 1.4 eV traps to a density >1 at.%. In the experiments reported here, identical samples were annealed at 1273 K for 6 h, and then partially loaded with deuterium, to examine the effect of annealing on these traps. The DIFFUSE [9] computer code was used to determine the density and energy of the traps controlling retention and release.

2. Experimental

2.1. Tungsten samples

The tungsten samples were cut from 3.18 mm diameter tungsten target rods irradiated with 800 MeV protons in LANSCE between September and November

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1996. Each sample was a thin disk, ~0.25 mm thick. The tungsten was formed by powder metallurgy and had an elemental composition of 99.96% tungsten with the major impurities being Mo (100 μg/g) and C and O (30 μg/g). Proton fluence ranged from $\sim 1.1\times10^{21}$ and $\sim 4\times10^{19}$ p/cm^2, with displacement rates of ~8 and ~0.3 dpa. Irradiation temperature was ~440 and ~310 K. A number of control samples were also made from unirradiated rods from the same lot.

2.2. Plasma discharge setup

Prior to deuterium glow discharge exposure, the samples were vacuum annealed to removed residual hydrogen isotopes formed during the irradiation. Annealing was done for ~1 h (control sample) and ~6 h (irradiated samples) at 1273 K. From earlier measurements [10], protium generation in the tungsten was expected to range from ~400 to ~2000 appm, with deuterium and tritium levels being lower.

Following annealing, each sample was exposed in a deuterium glow discharge using the setup shown in Fig. 1. The sample was placed on the tungsten rod electrode, which had the same diameter as the sample. Deuterium was continuously leaked into the system through a needle valve, while the chamber was being pumped. Deuterium pressure in the chamber was maintained between ~0.5 and 1 Torr. Discharge voltage was 1 kV; discharge current averaged about 100 μA. Each sample was exposed to the discharge for ~6 h for a total deuterium fluence of $\sim 2.5\times10^{20}$ D/cm^2. At 0.5 to 1 Torr pressure, the average energy of the deuterium ions striking the tungsten surface is estimated to be less than 100 eV. To accommodate this reduction in energy, the deuterium was assumed to be distributed only over the first 4 μm for the modeling.

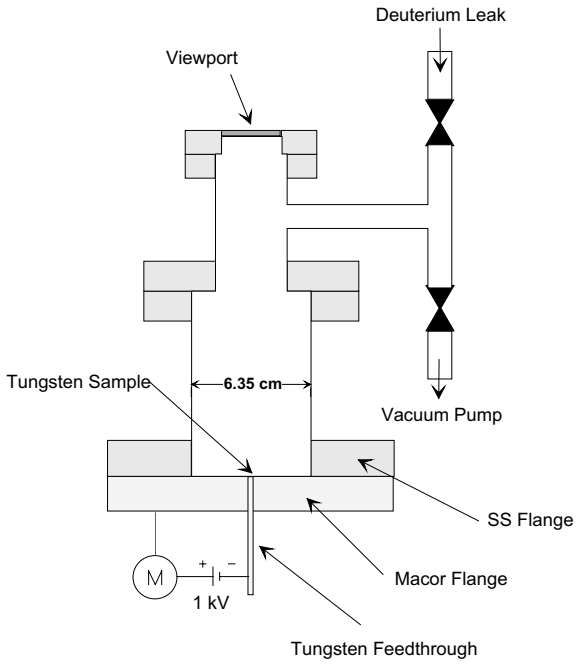

Fig. 1. Schematic diagram of deuterium discharge setup.

2.3. Gas analysis system

Hydrogen isotope release was measured using a specialized gas mass spectrometric system [11]. The samples were heated in a ceramic crucible whose temperature was linearly increased from ~300 to ~1430 K at a rate of ~50 K/min. Gas release was measured as a function of time using a quadrupole mass detector tuned for mass 2 (H_2), 3 (HD), and 4 (D_2) amu. Calibration of the system was accomplished using a hydrogen (H_2) leak source. Deuterium sensitivity was determined from measurements on a separate H_2/D_2 gas source. Sensitivity for HD was calculated assuming a $(1/M)^{1.25}$ relationship.

3. Results

For metals exposed to a hydrogen plasma, the parameters that determine both the amount of retained hydrogen and the subsequent release are diffusivity, recombination rate coefficient, and trapping energies and densities. Of the several formulas given in the literature for the diffusivity of hydrogen in tungsten, Causey and Venhaus [12] recommended the formula given by Frauenfelder [13] ($D = 4.1\times10^{-7}\exp(-0.39\text{ eV}/kT)$ m^2/s). Frauenfelder's experimental techniques were designed to minimize errors introduced by impurities and traps. The release rate of hydrogen from a surface is determined by the square of the surface concentration times the recombination rate coefficient. In the case of tungsten, it is not apparent that there is any holdup of hydrogen at the surface. Thus, it has been recommended [12], that an infinite value be assumed for the recombination rate coefficient, which is equivalent to assuming a boundary condition of $C = 0$ at the surface. The number of trap sites for hydrogen in tungsten is strongly affected by the thermal history of the sample. Unirradiated tungsten samples annealed at 1273 K are known to have significantly fewer trap sites than unannealed samples [1]. Experimentalists [1,7,14–17] have assumed various values for the trap energy in an effort to model their results on hydrogen isotope retention in tungsten. While the energy reported in these studies varied somewhat, a majority [1,7,14,15,17] have listed a trap at 1.4 eV as being the trap that is most important in controlling hydrogen retention and release.

Our modeling of the results included all aspects of the experiment that had an effect on the deuterium release

data. This included the 6-h glow discharge, the 3–5 days waiting period between the discharge exposure and the outgassing, and the outgassing itself. Thermal desorption spectra for the unirradiated tungsten is shown in Fig. 2. A very small shoulder on the left side of the main peak can be detected at ~450 K. Due to its very small size, no attempt was made to model the peak for this sample, however, this peak will be discussed at length for the two irradiated samples. The rest of the spectra consists of a major peak at ~530 K, and a smaller, broad peak at higher temperatures. As an initial attempt to fit the main peak, a single energy trap with a uniform distribution was assumed. To locate the peak at the correct temperature required a trap energy of ~1.0 eV. Not only was this an energy that had not been reported in the literature, but also the width of the fitted peak was far too great. A much closer fit to the experimental data was achieved by assuming 1.4 eV traps distributed over the first 30 nm with a concentration of 20 at.%. It is believed that these traps resulted from the cutting or machining of the specimens, and are more closely associated with surface defects than bulk defects. To account for the broad higher temperature peak, a uniform distribution of 1.4 eV traps located over the entire 300 μm thickness of the sample at a density of 2 appm was assumed. The overlay of the fitted data to the experimental results is also shown in Fig. 2.

The thermal desorption spectra for the two irradiated samples are shown in Figs. 3 and 4. The similarity of the two spectra is surprising. One sample was irradiated to a proton dose of ~0.3 dpa while the other sample saw a dose of ~8 dpa. It would be intuitive to assume the more heavily damaged sample to have a much greater trap density. This apparent inconsistency will be discussed at the end of this section. For modeling purposes, the results for the 0.3 dpa sample were used with the understanding that the desorption spectra for both irradiated samples are basically fit by the same parameter set.

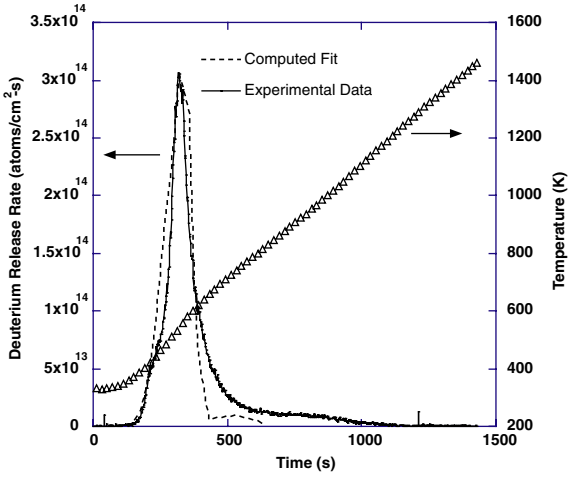

Fig. 2. Thermal desorption spectra and overlay of modeling data for unirradiated tungsten.

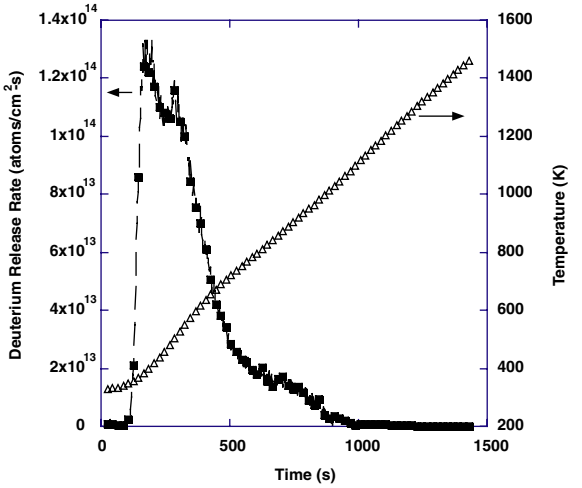

Fig. 3. Thermal desorption spectra for proton-irradiated tungsten (~0.3 dpa).

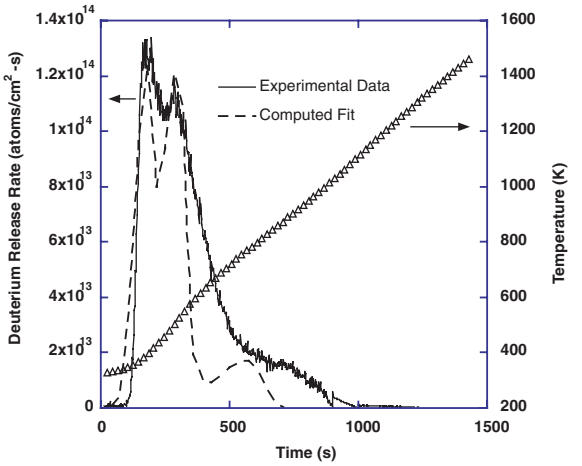

Fig. 4. Thermal desorption spectra and overlay of modeling data for proton-irradiated tungsten (~8 dpa).

The desorption spectra shows three peaks: a distinct peak at about 400 K; another distinct peak at 530 K; and a shoulder type peak centered at about 800 K. The second and third peaks are due to the same traps described for the unirradiated sample. For the DIFFUSE code, the assumption of a machining induced trap of 1.4 eV over the same 30 nm at a density of 8 at.% predicts a relatively sharp peak, closely resembling the experimental data. The lower trap density for this near-surface trap (8% vs. 20% for the unirradiated sample) is possibly due to the longer anneal at 1273 K (6 h vs. 1 h) for the

irradiated samples. The higher temperature peak was modeled assuming a uniform distribution of 1.4 eV traps at a density of 4 appm. This density is only slightly higher than for the unirradiated sample, and suggests that the anneal was very effective at removing irradiation induced traps. The inability to more accurately model this high temperature peak was likely due to a small fraction of deuterium also trapped at higher energy traps, perhaps chemisorbed on void surfaces.

The lowest temperature peak was the most interesting as it was almost totally absent for the unirradiated sample. This difference leads to the conclusion that the irradiation, or conditions present during the irradiation, significantly increased the responsible trap. Because these samples were irradiated with 800 MeV protons, the damage should be uniform throughout the relatively thin samples. Repeated modeling could not generate a release peak at this temperature using a uniformly distributed trap. Considering, however, that for the ~2.5 months that the tungsten was irradiated, it was immersed in water at a temperature of ~440 K. According to Fromm and Gebhardt [18], the diffusivity of oxygen in tungsten at this temperature is 1.5×10^{-16} cm^2/s. Thus, oxygen from the cooling water should have diffused ~0.6 μm into the sample during the proton irradiation. Assuming that the oxide related traps were uniformly distributed over the outer 0.6 μm, it was determined that a 0.95 eV trap at a density of 0.35 at.% gave a reasonable fit to the experimental data. The overlay of the DIFFUSE code output to the thermal desorption data can be seen in Fig. 4.

4. Discussion

Examining the overlay plots above, it is apparent that the sharp peaks of the fitted data do not match well the smooth curves of the experimental data. In the model, it was assumed that there was a uniform concentration of 1.4 eV traps over the first 30 nm of the sample. It is much more likely, however, that both the energy and concentration of the traps followed some distribution, with the traps being non-uniformly distributed over the first 100 nm, and most of the traps existing in the first 20–40 nm. While it was not practical to model the experimental data to that extent, the parameter values assumed in the present model do closely resemble reality. For example, it was not possible to replace the 1.4 eV traps with 1.2 or 1.6 eV traps, nor was it possible to assume the traps to be only in the first 1 nm or to be uniformly distributed.

The most surprising result of the present work was the absence of irradiation-induced traps in the irradiated samples. In earlier experiments [8] using identical samples, thermal desorption spectra were obtained for the protium already in the samples from the irradiation. To match that data, it was necessary to assume 1.4 eV traps at a concentration >1 at.%. In the present experiments, it was necessary to first anneal the irradiated samples to remove proton-generated deuterium and tritium that would have interfered with the signal from the deuterium implanted during the glow discharge exposure. From the work of Anderl et al. [1], it was known that annealing tungsten reduces the dislocation density on cell walls, with a one-to-one reduction in the 1.4 eV traps. The surprise was that a temperature of only 1273 K for 6 h could effectively remove all such traps from a highly irradiated tungsten sample. The results also suggest that hydrogen trapping at voids is not as prevalent as had earlier been assumed [7,14,17]. If voids had played an important role in the trapping of protium in the earlier [8] samples, then these traps would still be active in these later experiments, and the overall level of trapping would have been much higher. It is not possible to anneal out voids in tungsten by heating to only 1273 K [17], so any voids present would have still remained.

The high concentration of 1.4 eV traps in the near-surface region was also interesting. Many reports [15–17,19] on the thermal desorption of hydrogen isotopes from tungsten have noted low temperature release peaks, but none have suggested a local concentration of relatively high energy traps as being responsible. The resistance of these traps to removal by annealing is not understood. It must be assumed that the near-surface traps are different from the dislocation-controlled traps in the bulk.

The other non-uniform traps for hydrogen in the tungsten are suggested to be due to oxygen impurities that diffused into the tungsten during the proton exposure. Unfortunately, it was not possible to test the samples with analysis such as Auger Spectroscopy or Secondary Ion Mass Spectroscopy (SIMS). Poon et al. [20] have shown that oxygen can exist in the near surface of tungsten at relatively high concentrations. Oxygen is typically found as an impurity in less clean tungsten, and may be the source of moderate energy trap sites reported in some papers [15–17,19].

5. Conclusions

Thermal desorption spectra of tungsten after exposure to a deuterium glow discharge have been measured. The desorption spectrum of an unirradiated sample was compared to those for samples exposed to 0.3 and 8 dpa proton dose. The two proton irradiated samples were annealed at 1273 K for ~6 h prior to the deuterium glow discharge exposure to remove hydrogen isotope impurities generated by the proton irradiation.

The deuterium release from the unirradiated sample was dominated by a peak at about 550 K that appeared to come from a high concentration of 1.4 eV traps very

near the surface. Annealing at 1273 K for 1 h prior to the measurements, combined with the purity of the sample, appears to have minimized the concentration of uniform 1.4 eV traps seen in some tungsten. The near-surface trapping is thought to be associated with damage (e.g., line defects) from the cutting process.

The annealing appears to have been very successful in removing the high concentration of uniform 1.4 eV traps created by the irradiation exposure. The desorption spectra of both samples was dominated by release from near-surface 1.4 eV traps, a low concentration of uniform 1.4 eV traps, and a 0.95 eV trap thought to be associated with oxygen that diffused into the tungsten samples during the proton exposure.

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